

## \* NOTICES \*

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

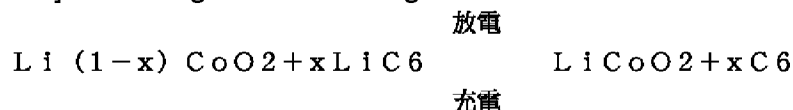
[Field of the Invention]This invention relates to a nonaqueous electrolyte secondary battery.

[0002]

[Description of the Prior Art]In recent years, development of an advanced battery is desired with development of portable electronic equipment. A lithium secondary battery is mentioned as what fills this request. Lithium shows the most \*\*\*\* potential in metal, and since specific gravity is also as small as 0.534, the lithium secondary battery using this as negative electrode active material of a cell can expect a big energy density compared with the cell which uses conventional solution. However, since the dendrite of lithium deposits if charge and discharge are repeated, a lithium secondary battery has a problem of the safety by cycle degradation or an internal short circuit, and is not put in practical use except for the coin type cell.

[0003]On the other hand, cobalt acid lithium which is a multiple oxide which has a carbon material in a negative electrode and has the layer structure in an anode, The lithium ion battery using the organic electrolysis liquid which consists of an organic solvent which dissolved lithium salt in the electrolysis solution is put in practical use as a cell with operating potential high compared with the cell which uses conventional solution, and a high energy density.

[0004]The charge-and-discharge reaction of a lithium ion battery is shown below.



Lithium in an anode serves as ion by charge, it begins to melt into an electrolysis solution, and occlusion of the lithium ion in an electrolysis solution is carried out to carbon of a negative electrode. A reverse reaction arises at the time of discharge.

[0005]Although the theoretical capacity of Li(1-x) CoO<sub>2</sub> used for positive active material is 274

mAh/g ( $x=0$ ), in order to perform charge 100%, the high tension beyond 4.8V is needed in the state of a cell. However, if it charges above said pressure value, in order for disassembly of an electrolysis solution to arise and to cause the fall of the reversible capacitance by a phase change further, by the actual cell, upper limit voltage was specified to 4.1-4.2V, and positive active material is used by  $x=$  around 0.5 stable zones.

[0006] Since lithium always exists in the form of ion, deposits metal lithium further in process of this reaction and a dendrite is not produced, compared with a lithium cell, safety is improving greatly.

[0007] However, since it has that it is a cell of high energy density, and inflammable organic electrolysis liquid, to safety, careful consideration is needed. For example, when black lead is used as a carbon material of a negative electrode, although it is 372 mAh/g, since the theoretical capacity has the potential of a charging end term with high charge depth close to the potential of lithium, at the time of charge, metal lithium deposits on a black lead surface, and it causes formation of a dendrite to it. Therefore, in order not to spoil safety, charge depth is made about 70% and it uses.

[0008]

[Problem(s) to be Solved by the Invention] The lithium ion battery which uses the carbon material for the negative electrode has the theoretical capacity and cell voltage of a negative electrode lower than the lithium cell which used metal lithium for the negative electrode. Therefore, in order to raise the capacity of a negative electrode in a lithium ion battery, charge depth is raised and the method of depositing metal lithium on the carbon material surface of a negative electrode at a charging end term is taken. However, the method of making charge depth of a negative electrode still higher is needed, without producing a dendrite so that safety may not be spoiled. However, as stated previously, when charge depth was made high in the conventional negative pole material, there was a problem that a dendrite was formed and safety was spoiled.

[0009] The conventional carbon material is used for a negative electrode, and if it charges by making the charge depth deep, the metal lithium which serves as a core on a carbon material surface first at a charging end term deposits. This metal lithium has the high activity over a deposit of metal lithium compared with a surrounding carbon material, and to eye others. When it furthermore charged, without depositing uniformly on the whole surface of a carbon material, metal lithium deposited preferentially focusing on the core, and metal lithium had the problem that formation of a dendrite advanced.

[0010] In view of the above problem, an object using the negative electrode which can deposit metal lithium on the surface of a carbon material without spoiling safety of this invention is to enable high capacity-ization of a nonaqueous electrolyte secondary battery.

[0011]

[Means for Solving the Problem]In a nonaqueous electrolyte secondary battery with which this invention uses for a negative electrode a carbon material in which it comes to support metal particles in order to attain this purpose, Metal particles Copper (Cu). Or nickel (nickel), iron (Fe), chromium (Cr), titanium (Ti), zirconium (Zr), or vanadium (V), beryllium (Be), potassium (K), plutonium (Pu), niobium (Nb), or these metal. By considering it as a nonaqueous electrolyte secondary battery being an included alloy. Without not spoiling safety but a dendrite arising on a carbon material surface further, even if it makes charge depth of a negative electrode still higher, make it possible to deposit metal lithium uniformly on a surface of a carbon material, and let a problem be a solution plug like the above.

[0012]If it is in manufacture of a nonaqueous electrolyte secondary battery of this invention, a manufacturing method characterized by making this negative electrode support the above-mentioned metal particles after producing a negative electrode using a carbon material -- or a carbon material is made to support the above-mentioned metal particles beforehand, and a manufacturing method producing a negative electrode using this carbon material is used.

[0013]It is a nonaqueous electrolyte secondary battery preferably characterized by the above-mentioned support being high distribution support.

[0014]In order to solve the above-mentioned technical problem, in a charging state, it is supposed that the above-mentioned nonaqueous electrolyte secondary battery depositing metal lithium on the carbon material surface, and using for it is provided. It is supposed that the above-mentioned nonaqueous electrolyte secondary battery using charge depth of a negative electrode as not less than 80% is provided.

[0015]

[Embodiment of the Invention]As a carbon material, corks, meso carbon micro beads (MCMB), A meso FIZU pitch based carbon fiber, pyrolysis vapor-phase-epitaxy carbon fiber, a phenol resin baking body, The graphite material represented by the carbonaceous material, an artificial graphite and natural graphite, the graphitization MCMB, graphitization mesophase pitch system carbon fiber, and graphite whisker which are represented by polyacrylonitrile (PAN) system carbon fiber, a pseudo-isotropic carbon, and furfuryl-alcohol-resin baked carbon can be used.

[0016]The shape of a carbon material has the goodness of the handling in the case of electrode formation, and the diffusibility of the reaction surface area after electrode formation, or a lithium ion to preferred powder state.

[0017]As metal particles, it is with copper (Cu), nickel (nickel), iron (Fe), or chromium (Cr). Compared with a carbon material, these metal particles show high activity to a deposit of metal lithium, and are still cheaper compared with metal lithium, and preferred as a negative pole material. Furthermore, titanium (Ti), zirconium (Zr), or vanadium (V), beryllium (Be), potassium (K), plutonium (Pu), or niobium (Nb) can be used.

[0018]The alloy containing the above-mentioned metal may be sufficient as metal particles, and a mixture may be sufficient as them.

[0019]As for the mean particle diameter, in order that metal particles may improve the activity over a deposit of metal lithium, it is still more preferably preferred that it is 50 Å or less 100 Å or less.

[0020]As for these metal particles, since metal lithium deposits on a carbon material surface uniformly at a charging end term, high-distributing to the carbon material is preferred.

[0021]With the carbon material in which it comes to carry out high distribution support of the metal particles, the microatomized metal particles distribute uniformly on this carbon material surface.

[0022]In order that metal particles may show high activity to a deposit of metal lithium compared with metal lithium compared with a carbon material further, metal lithium deposits at a charging end term with the priority to the metal particles supported to the carbon material. Therefore, if the carbon material is made to high-distribute metal particles, it will become possible here to deposit a carbon material surface of metal lithium uniformly.

[0023]the black lead which supported silver (Ag) to the negative electrode of the lithium ion battery -- \*\*\*\* -- things are announced by Hitoshi Honbo -- \*\*\*\* (the 38th cell debates, 225, (1997)) -- this being supporting Ag and, It aims at improving the current collection nature fall between the active materials considered to be the causes of life degradation, and completely differs from the purpose of this invention. A part exists in the state of LiAg, without emitting thoroughly the lithium in which occlusion of the lithium was carried out by the alloying reaction of LiAg on the occasion of charge, and occlusion of Ag was carried out on the other hand at the time of discharge. Therefore, it has a problem to which capacity falls compared with the case where metal lithium is deposited in a graphite surface.

[0024]Therefore, the metal particles supported to a carbon material need to use what does not form lithium and an alloy or it is hard to form. Because, if occlusion of the metal particles is carried out to lithium in the form of an alloy at the time of charge, the lithium by which occlusion was carried out will remain in the state of an alloy in part, without being emitted thoroughly, and service capacity will fall to the carbon material surface compared with the case where metal lithium is deposited.

[0025]Although it is the charge depth of a negative electrode here, in order that a dendrite might grow conventionally, were pressing down the charge depth of the negative electrode to about 70%, but. In the rechargeable battery concerning this invention, growth of a dendrite is not accepted as for not less than 80% in the charge depth of a negative electrode, but the capacity of a carbon material can be utilized for the maximum.

[0026]When charge depth is made not less than 80%, a deposit of metal lithium may also take place to a negative electrode, but since it deposits uniformly on the surface of a carbon

material, this metal lithium does not lead to growth of a dendrite, but it can raise capacity, without spoiling safety.

[0027]Since metal lithium deposits uniformly on the surface of a carbon material when charge depth of a negative electrode is made not less than 100% or metal lithium is positively deposited on the carbon material surface, Growth of a dendrite does not take place but can be used as the nonaqueous electrolyte secondary battery of the high capacity which does not spoil safety.

[0028]Although it is the maximum of charge depth, in order to prevent the fall of the current collection nature resulting from expansion contraction of the negative electrode accompanying the charge and discharge by depositing metal lithium on the carbon material surface, it is preferred to consider it as 150% or less still more preferably a maximum of 200%.

[0029]Charge depth is a charge at the time of making the interchange of lithium or the theoretical capacity (mAh/g) of ration in a carbon material into 100%, for example, the charge used as 372 mAh/g is made into 100% in black lead. however, an amorphous system -- in a carbon material, it is not this limitation.

[0030]

[Example](Example 1) This invention is hereafter explained using a suitable example.

[0031]nickel -- 10wt% -- graphitization MCMB 82.7wt% which carried out quantity distribution support, poly FUKKA vinylidene (PVdF) 8.2wt%, applied what mixed N-methyl-2-pyrrolidone (NMP) 9.1wt% on 14-micrometer-thick copper foil, it was made to dry at 150 \*\*, and NMP was evaporated. After performing the above operation to both sides of copper foil, it pressed and was considered as the negative electrode. The thickness of the negative electrode after a press was 120 micrometers.

[0032]Next, cobalt-acid-lithium 65wt%, acetylene black 6wt%, the solution which contains orthophosphoric acid H<sub>3</sub>P O<sub>4</sub> to purified water 20wt% which dissolved polyvinyl alcohol 9wt% 0.0002M was applied on 20-micrometer-thick aluminium foil, it dried at 90 \*\*, and water was evaporated. It pressed, after carrying out the above operation to both sides of aluminium foil, and it was considered as the anode. The thickness of the anode after a press was 170 micrometers.

[0033]Right [ these ] and negative electrode plates, and a 26-micrometer-thick polypropylene fine porous separator were rolled in piles, it inserted into the stainless case (47.0 mm in height, 22.2 mm in width, and 6.4 mm in thickness), and the square-shaped cell was assembled. Then, 2.5g of mixed (volume ratio 1:1) electrolysis solutions of ethylene carbonate containing LiPF<sub>6</sub> of 1M and diethyl carbonate were added, and it was considered as the cell (A) of the example of this invention. Here, the theoretical capacity of the negative electrode of a cell (A) adjusted the insertion amount of each electrode so that the theoretical capacity of 400mAh and an anode might serve as 800mAh.

[0034](Comparative example 1) Except having used for the negative electrode what mixed N-methyl-2-pyrrolidone (NMP) 10wt% poly FUKKA vinylidene (PVdF) 9wt% graphitization MCMB 81wt%, it was made the same as Example 1, and was considered as the cell (B) of the comparative example. Here, the theoretical capacity of the negative electrode of a cell (B) adjusted the insertion amount of each electrode so that the theoretical capacity of 400mAh and an anode might serve as 800mAh.

[0035]As the theoretical capacity of the negative electrode of these cells A and B and an anode shows, when the charge depth of an anode is 50%, the charge depth of a negative electrode will be 100%. In 20 \*\*, these cells were discharged to 2.75V with the current of 1CA, after having charged by 0.5CmA constant current, and charging with the constant voltage of 4.2V continuously for 2 hours. By charging on this condition, as for the charge depth of an anode, the charge depth of a negative electrode will be 102% 51%. This charge and discharge were repeated and the cycle life property of the cell was measured. The result of the capacitance retention and the charging and discharging cycle which set early capacity to 100 is shown in drawing 1.

[0036]From drawing 1, when the cell (B) of a comparative example repeats charge and discharge, as for the cell of this invention (A), the fall of capacity is hardly seen to the capacity falling. Metal lithium deposits uniformly [ the cell of this invention (A) ] on the surface of the graphitization MCMB of a negative electrode to the cell (B) of a comparative example being repeating charge and discharge, the dendrite of lithium depositing in a negative electrode, a fine short circuit producing this inside a cell, and capacity falling.

It is because formation of the dendrite has not arisen.

[0037]

[Effect of the Invention]As stated above, by using for the negative electrode of a nonaqueous electrolyte secondary battery the carbon material in which it comes to support the metal particles concerning this invention, it becomes possible to deposit metal lithium uniformly on the surface of a carbon material at a charging end term, and formation of a dendrite can be prevented. Therefore, high capacity-ization of a nonaqueous electrolyte secondary battery is attained, without spoiling safety.

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[Translation done.]